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# Temperature Gating of the Ring-Opening Process in Diarylethene Molecular Switches\*\*

By Diana Dulić,\* Tibor Kudernac, Audrius Pužys, Ben L. Feringa,\* and Bart J. van Wees

Organic photochromic compounds that allow reversible modulation of physical properties by using an external trigger are very promising candidates for optoelectronic devices,<sup>[1]</sup> high-density optical (multicolor) memories,<sup>[2]</sup> addressable polymers,<sup>[3]</sup> and, in general, smart materials.<sup>[4]</sup> Because of the excellent thermal stability of both open-ring and closed-ring isomers, and because of their fatigue-resistive properties, diarylethenes deserve special interest.<sup>[1-5]</sup> By using these molecules, novel photoswitching effects, such as changes in fluorescence intensity and wavelength,<sup>[6-13]</sup> electrochemical properties,<sup>[14]</sup> optical rotation,<sup>[15]</sup> magnetic properties,<sup>[16]</sup> electron-transfer interactions,<sup>[17]</sup> and conductance<sup>[18]</sup> have been demonstrated. Photoswitching effects are based on the reorganization of the  $\pi$ -conjugated backbone of the molecule that consequently leads to different physical properties. Knowledge of the vital factors governing photochromic processes is essential for future utilization of diarylethenes as smart materials as well as for a fundamental understanding of the photoprocesses involved. Hence, temperature-dependent studies are necessary to reveal new aspects and limits of the switching process, as previously shown by measurements at elevated temperatures.<sup>[19]</sup> Additionally, determining possible switching restrictions at low temperatures is particularly important in view of carrying out con-

ductance measurements at the single-molecular level, which are restricted at room temperature because of the high mobility of the gold atoms constituting the electrodes in this type of experiment. In order to achieve stability of the metal/molecule/metal system it is often necessary to perform measurements at low temperatures.<sup>[20]</sup>

Herein, we explore the temperature dependence of the photochemical behavior of dithienylcyclopentenes. We report the suppression of the ring-opening process with decreasing temperature, leading to the complete absence of the photoreaction below a cutoff temperature. By contrast, we demonstrate that the reverse ring-closure process shows no significant temperature dependence above 115 K. These observations of the temperature dependence for the ring-opening process are essential to understand the behavior of these molecular switches before they can be used in advanced technological applications. The theoretical description of the ring-opening process is not completely understood. Furthermore, the observed suppression of the ring opening might have important implications for gating of photochromic processes. Like for other photoreactions that have a photostationary state with less than 100% product, the ring-closure process for diarylethenes is accompanied by ring opening, because both forms have absorption peaks in the UV region, hence decreasing total conversions.<sup>[21]</sup> On the other hand, if ring opening can be blocked, total conversion increases.<sup>[22]</sup>

Two representative examples of dithienylcyclopentene photochromic switches have been investigated, the hexafluoro **F** (shown in Scheme 1 upper panel), and hexahydro **H** (Scheme 1 lower panel) switch,<sup>[23]</sup> both consisting of a central switching unit. In the **H** switch fluorines are replaced with hydrogens, and the two thiophene rings at the C5' positions of the switching unit are replaced with phenyl groups. Both compounds have a single acetyl-protected thiol group. When the molecule is in closed form it has an extended  $\pi$ -conjugated system. Upon exposure to visible light with a wavelength in the range  $500 \text{ nm} < \lambda < 700 \text{ nm}$ , the molecule switches from closed to open form. In the open form, the  $\pi$ -conjugation of the central ring is broken.

The UV-vis absorption spectra at 115 K and 290 K of the switches in isopentane solution are shown in Figure 1. The broad absorption bands with a maximum at  $\lambda = 590 \text{ nm}$  for **F<sub>c</sub>**, and  $\lambda = 537 \text{ nm}$  for **H<sub>c</sub>** are characteristic of the closed form of the switch. At low temperature the vibrational structure in the absorption spectra becomes more apparent, resulting in a sharpening of the absorption band and distinct absorption maxima can be recognized.

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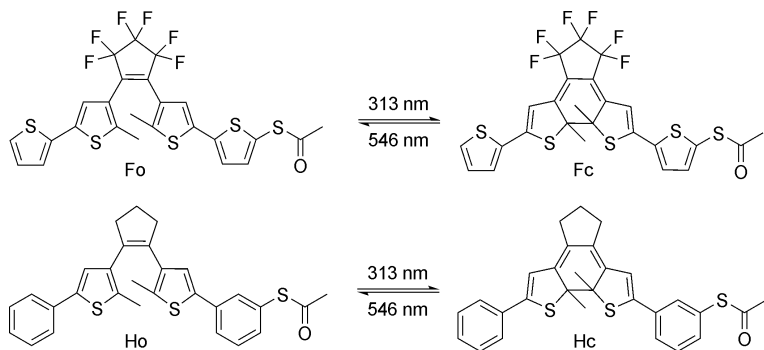
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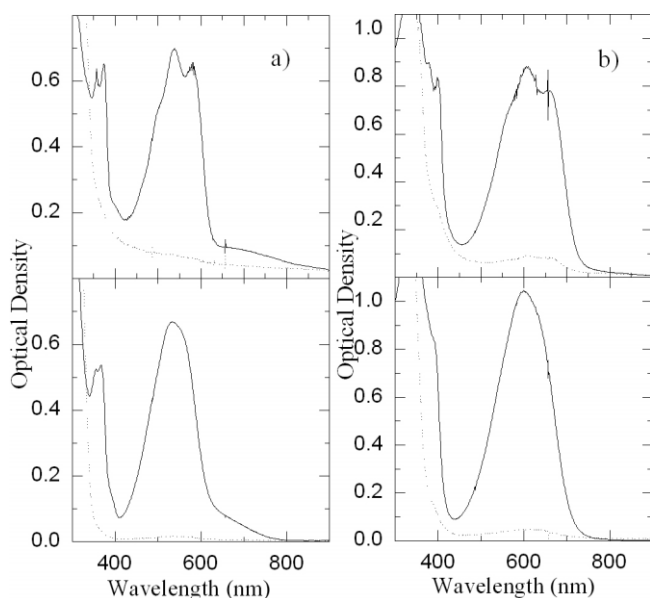
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**Scheme 1.** Hexafluoro **F** (upper panel), and hexahydro **H** photochromic molecular switch, in the open form  $F_o$ ,  $H_o$  (left side) and closed form  $F_c$ ,  $H_c$  (right side). By exposing the molecule to visible light ( $500 \text{ nm} < \lambda_1 < 700 \text{ nm}$ ), the molecule will switch from closed to open. The molecule can be switched back to the closed state by exposing it to UV light ( $300 \text{ nm} < \lambda_2 < 400 \text{ nm}$ ).



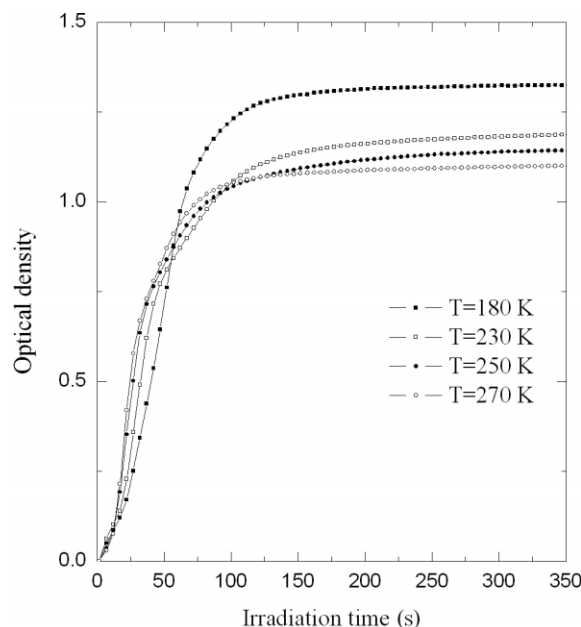
**Figure 1.** Absorption spectra of the molecular switches: a) **H** switches in isopentane at a concentration of  $7.94 \times 10^{-5} \text{ mol L}^{-1}$ ; the solid line represents the closed form, and the dashed line represents the open form. The upper panel measurements were taken at 115 K (isopentane at 115 K was used as a reference), and the lower panel measurements at 290 K (isopentane at 290 K was used as a reference); b) **F** switches in isopentane at a concentration of  $6.07 \times 10^{-5} \text{ mol L}^{-1}$ ; the solid line represents the closed form, and the dashed line represents the open form. The upper panel measurements were taken at 115 K, and the lower panel measurements at 290 K.

In order to explore the effect of temperature on switching efficiency, the kinetics of the switching process were examined (for both ring closure and ring opening). At each temperature a solution containing the switch in the open form was used as a reference spectrum (blank). Therefore, any absorption changes induced by radiation are related to the evolution of the closed form. The time evolution of the differential absorption of the closed form was monitored to follow the kinetics

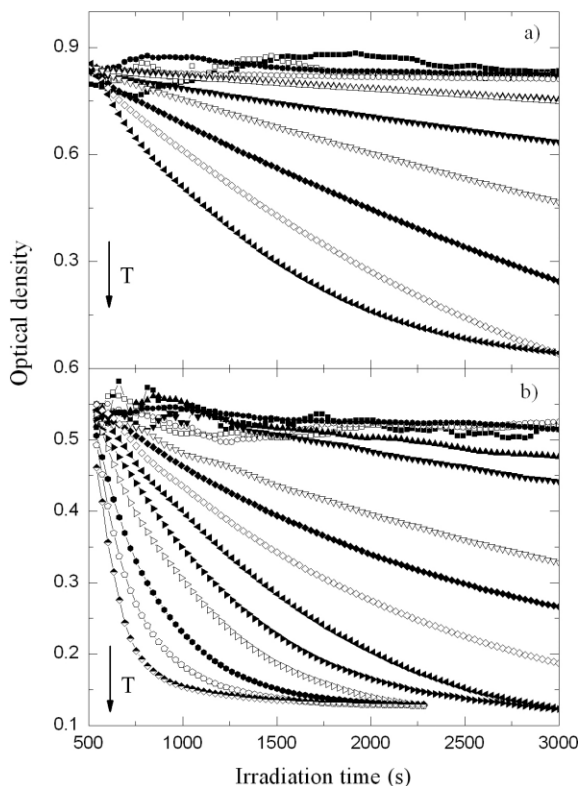
of the switching reactions. To promote ring closure, UV light with  $\lambda = 313 \text{ nm}$  was used until the photo-stationary state was reached.<sup>[24]</sup> The kinetics of this process for different temperatures are represented in Figure 2 for the **H** switch. For each temperature a fresh solution was used. The data points are plotted for the wavelength corresponding to the maximum absorption of the closed form ( $\lambda = 537 \text{ nm}$ ). The results demonstrate that the ring-closure process is effectively temperature independent in the measured temperature range.

Similar behavior was observed for the **F** switch (monitored at  $\lambda = 590 \text{ nm}$ ). The kinetics of the ring opening were followed at the same wavelengths as ring closing during irradiation with visible light at  $\lambda = 546 \text{ nm}$ . In contrast to the ring closure, the ring-opening process was strongly temperature dependent, as shown in Figure 3. For both the **F** and **H** switch the ring-opening process was suppressed completely at ca. 130 K and at around 120 K, respectively. For each temperature the data points were plotted on a logarithmic scale, and the linear initial portion of the curve was fitted to determine the rate ( $K(T)$ ; dependent on temperature) of ring opening. In Figure 4 the logarithm of the rate is plotted versus inverse temperature. The curves show two distinct components, a temperature-dependent region where photochemical ring opening is observed and a temperature-independent region where no photochemistry is observed.

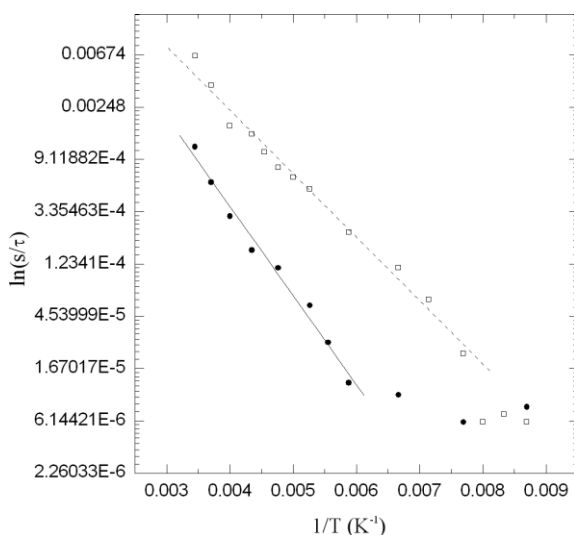
From the slope of the temperature-dependent component of the curve the thermal barrier of the ring opening is obtained. Although the observed rate of ring opening is dependent on the intensity of the light source, the exponential com-



**Figure 2.** Kinetics of the ring closure for **H** switches obtained at  $\lambda = 537 \text{ nm}$  for different temperatures.



**Figure 3.** Temperature-dependent kinetics of the ring-opening process: a) F switches obtained at  $\lambda=590$  nm. Temperatures: 115, 130, 150, 170, 180, 190, 210, 230, 250, 270, and 290 K; b) H switches at  $\lambda=537$  nm. Temperatures: 115, 120, 125, 130, 140, 150, 170, 180, 190, 200, 210, 220, 230, 250, 270, and 290 K. The curves are brought to the same value along the y-axis for clarity reasons.

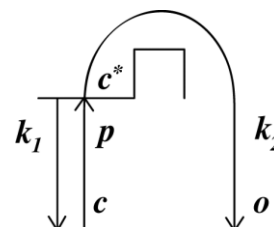


**Figure 4.** Arrhenius plot for F (squares), and H (circles) switches with corresponding linear fits.

ponent of the fit is intensity independent. This has an important implication for the determination of activation energies. The validity of the approach taken is not immediately ob-

vious. In the following section, we demonstrate that our approximation is justified under the low irradiation intensities employed.

In Scheme 2 we show an illustrative diagram of the energy levels involved in the ring-opening process. Ring opening of the closed form requires first the molecule being promoted to



**Scheme 2.** Sketch of the energy levels of the ring-opening process, where  $c$ ,  $c^*$  and  $o$  represent populations of the ground state and excited state of the closed form and ground state of the open form, respectively.  $p$  is the pump rate and  $k_1$  and  $k_2$  are the rates from excited to closed and excited to open state.

the THEXI state (thermally equilibrated excited state) upon irradiation with visible light, followed by the crossing of a thermal barrier. Semi-empirical quantum-chemical computational methods<sup>[18b]</sup> have predicted the existence of this barrier. So far, experimentally the thermal barrier and its importance has not been studied in detail; experimental studies have only been performed at elevated temperatures with very few data points.<sup>[19]</sup>

The full set of differential equations that describes the ring-opening dynamics is

$$\frac{dc(t)}{dt} = -p \cdot c(t) + k_1 \cdot c^*(t) \quad (1)$$

$$\frac{dc^*(t)}{dt} = p \cdot c(t) - k_1 \cdot c^*(t) - k_2 \cdot c^*(t) \quad (2)$$

$$\frac{do(t)}{dt} = k_2 \cdot c^*(t) \quad (3)$$

where  $c(t)$ ,  $c^*(t)$ , and  $o(t)$  represent populations of the ground state and excited state of the closed form and ground state of the open form, respectively.  $p = \sigma_0 I$  is the pump rate,  $\sigma_0$  is absorption cross section, and  $I$  is the intensity of the light.  $k_1$  and  $k_2$  are the rates from excited to closed and excited to open state, respectively, where  $k_2 = k_2(0) \exp(-\Delta E / (k_B T))$ , with  $\Delta E$  being the activation energy,  $k_B$  the Boltzmann constant, and  $T$  the temperature. At stationary conditions when the pump intensity is very weak, the population of the excited state of the molecules in the closed form is proportional to the population of the ground state,  $c^*(t) = a c(t)$ , where  $a \ll 1$ . With this approximation Equations 1 and 2 are reduced to

$$\frac{dc^*(t)}{dt} = -\frac{dc(t)}{dt} - k_2 \cdot c^*(t) \quad (4)$$

$$\frac{dc(t)}{dt} = -c(t) \cdot \frac{a}{a+1} \cdot k_2 \quad (5)$$

For a  $\ll 1$ ,  $1+a \approx a$ , and Equation 5 becomes

$$\frac{dc(t)}{dt} = -c(t) \cdot a \cdot k_2 \quad (6)$$

with a solution of

$$c(t) = c_0 \exp(-a \cdot k_2 \cdot t) \quad (7)$$

By fitting our experimental data we obtain  $k(t) = k_2 a$ . Because  $a$  does not depend on temperature, we can write

$$K(t) = k_2^0 \cdot a \cdot \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (8)$$

$$\ln(K(t)) = \ln(k_2^0 \cdot a) - \frac{\Delta E}{k_B T} \quad (9)$$

Therefore the data presented in Figure 4 can be fitted with a single exponent. The Arrhenius plot allows the determination of the activation energies of  $\Delta E = 147$  meV for the **F** switch, and  $\Delta E = 104$  meV for the **H** switch. The different values for the activation energies indicate that the thermal barrier is sensitive to changes in molecular structure. It implies that further understanding of the barrier is necessary for optimization of the switching properties. In particular finding a way to reduce the barrier by an order of magnitude would significantly increase the switching rate (by a factor of 1000).

In conclusion, UV-vis kinetics experiments over the temperature range 115–290 K for **F** and **H** dithienylcyclopentene-based photochromic switches reveal a key parameter associated with the reversibility of these molecular systems. For the first time, we show that whereas the ring-closing process shows little temperature dependence, photochemical ring opening is strongly temperature dependent and below ca. 130 K, the photochemistry is effectively suppressed. The strong temperature dependence of the ring opening implies that variation of temperature might be used for the gating of the photochromic behavior of diarylethenes.

## Experimental

UV-vis absorption spectra were measured by using a HP 8453 diode array UV-vis spectrometer. In principle, the light from the spectrometer interacts with the molecules causing a photoreaction. However, repetitive acquisitions showed no detectable changes in the absorption spectra which we attribute to the weak intensity of the source. A high-pressure mercury lamp (200 W, Oriol) was used with 10 nm FWHM (full-width half maximum) band-pass filters to switch the molecules from the open to the closed state and vice versa. Light beams with power densities of  $0.094 \text{ mW cm}^{-2}$  for  $\lambda = 546$  nm were employed for ring opening, and  $0.00354 \text{ mW cm}^{-2}$  for  $\lambda = 313$  nm to achieve ring closure. The powers were measured before and after the experiment for each temperature. In order to minimize artifacts due to diffusion, the entire sample volume ( $1 \text{ cm}^3$ ) was irradiated. Temperature-dependent measurements were performed between 115 and 290 K, using a liquid-nitrogen-cooled optical cryostat (Optistat, Oxford instruments). Isopentane solutions of both compounds,

with a concentration of  $6.07 \times 10^{-5} \text{ mol L}^{-1}$  for the **F** switch, and  $7.94 \times 10^{-5} \text{ mol L}^{-1}$  for the **H** switch, were used.

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